

Research paper

Complex gas hydrate system in a gas chimney, South China Sea

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ABSTRACT

Gas hydrates and deep-sea cold seeps are of interest to industry and academia for several reasons, including their implications for offshore geohazards and unconventional resources, and for global climate change and carbon cycling. Guangzhou Marine Geological Survey (GMGS) implemented its fifth gas hydrate drilling expedition in the Qiongdongnan Sea Area (QDN-SA) of the northern South China Sea (SCS) from June to September 2018. Multidisciplinary investigations, including Logging While Drilling (LWD), pressure and non-pressure coring, gas composition analyses, in situ temperature and permeability measurements, pore water geochemical analyses, and a regional seismic survey, reveal a complex distribution of gas hydrate within a vertical chimney structure. LWD profiles record high resistivity anomalies and high P-wave velocity variations at 9–174 mbsf, suggesting the coexistence of free gas and gas hydrate in the sediment column throughout the investigated gas chimney. Hydrate-bound and void gas is an admixture of methane (70.1%–98.3%) and heavier hydrocarbons (C_2H_6 : 0.16%–17.59%, C_3H_8 : 0.05%–9.88%, $i-C_4H_{10}$: < 0.001%–2.06%, $n-C_4H_{10}$: < 0.001%–0.85%, $i-C_5H_{12}$: < 0.001%–0.12%, $n-C_5H_{12}$: < 0.001%–0.02%), indicating a thermogenic origin for the gas. Based on the high content of C_2+ hydrocarbons in the gas composition, it is suggested that sII/sH gas hydrate exists in the study area. The gas chimney is interpreted to provide efficient pathways for fluid migration from an intermediate gas reservoir below the BSR to the gas hydrate stability zone (GHSZ). Gas hydrate crystallization decreases the permeability of the sediment, impeding fluid flowing into the upper sediment layers. Bivalve fragments embedded within carbonate rocks were recovered at the seafloor and multiple levels at two main sediment levels of 3 mbsf and ~54 mbsf, indicating recurrent seepage activity.

1. Introduction

Gas hydrates are crystalline compounds composed of water and gas molecules under high pressure and low temperature (Sloan, 2003). They are widely distributed in the deep water continental margins and in permafrost areas (Kvenvolden et al., 1993). As a potential future energy resource (Mordis et al., 2013) and carbon reservoir of global importance (Dickens, 2003), gas hydrates have been intensively investigated (Pape et al., 2011; Sha et al., 2015; Torres et al., 2008; Tréhu et al., 2004). The occurrence of gas hydrate and its distribution, concentration and morphology within sediments is controlled by several factors, such as fluid migration pathways, gas sources, tectonic settings and sediment type (Abegg et al., 2008). Mud volcano conduits, gas chimneys, faults and shallow fractures provide efficient pathways for fluid migrating from deep subsurface to form gas hydrate (Sultan et al.,

2014; Zhang et al., 2018). Massive gas hydrates commonly occur as veins and nodules in association with faults and fractures (Cook et al., 2008; Weinberger and Brown, 2006), whereas layered gas hydrates are associated with horizontal fluid migration in more permeable beds (Tréhu et al., 2004). In sediment where methane migrates via diffusion, gas hydrates usually occur disseminated in the sediment pores.

Deep sea cold seeps are sites where fluids are emitted from seafloor sediments into the ocean (Sibuet and Olu, 1998). In contrast to hydrothermal vents (Ili et al., 2001), the temperature of fluids in cold seep systems is similar to that of the ambient water. Seeping fluids are usually enriched in low molecular mass hydrocarbons, mainly methane. However, other gases, such as carbon dioxide, hydrogen sulfide and heavier hydrocarbons (C_2+) might also be present depending on the gas source (Blinova et al., 2003; Pape et al., 2011). Authigenic carbonates which form as a by-product of sulfate reduction and methane

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oxidation, are typically observed at cold seeps (Bayon et al., 2013). In active seeps, the flux of hydrogen sulfide and methane supports chemosynthetic organisms such as tubeworms and bivalves (Levin, 2005). Eventually, authigenic carbonates and seep-related bivalves become buried due to sedimentation. Although cold seeps at the seafloor (i.e. active at present-day or recently active) have been the subjects of many studies (Blumenberg et al., 2015; Bohrmann et al., 1998; Feng et al., 2014; Loyd et al., 2016), paleo-cold seeps which were active in the geological past and are represented by antigenic carbonates and bivalve fragments, have been rarely reported due to the difficulty in acquiring samples (Li et al., 2018). However, buried carbonate crusts may provide valuable information about the nature of fluid flux through the seafloor over time and gas hydrate formation and dissociation in relation to climate-driven variations in bottom water temperatures and sea level (Bayon et al., 2013; Berndt et al., 2014; Bohrmann et al., 1998; Han et al., 2014).

China is giving great attention to marine gas hydrate investigation and exploitation (Li et al., 2018). From 2007 to 2016, Guangzhou Marine Geological Survey (GMGS) implemented four gas hydrate drilling expeditions in the eastern Pearl River Mouth Basin (PRMB) (Sha et al., 2015; Zhang et al., 2015) and Shenhu Sea Area (SSA) (Wang et al., 2011) of the South China Sea. These expeditions obtained sediment cores and gas hydrate samples as well as comprehensive geophysical logging-while-drilling (LWD) data. Gas hydrate nodules and veins were recovered from the eastern PRMB in 2013, while disseminated (i.e. pore-filling) gas hydrates were recovered from the SSA in 2015 and 2016. Molecular and isotopic compositions showed that the hydrate-bound gases were mainly biogenic with minor thermogenic gas (Liu et al., 2012). Raman spectroscopy analysis revealed that gas hydrates from PRMB and SSA are both sI (Liu et al., 2012, 2015). However, a recent study has shown that sII hydrate co-exists with sI hydrate in the SSA (Wei et al., 2018).

In this paper, we present the first results from the fifth gas hydrate drilling expedition (GMGS5) in the Qiongdongnan Sea area (QDN-SA) of the South China Sea, from drilling site QDN-W08-2018 (Fig. 1). By drilling through a gas chimney, we obtained information on gas hydrate occurrence (distribution in sediments, gas composition, and hydrate structure), geothermal gradient, permeability, pore water chemistry and the seep-related authigenic carbonates. These field data support a preliminary discussion of the sources and migration pathways of fluids from depth, the dynamics of gas hydrate formation within the gas chimney system and the nature of seepage activity through time.

2. Geological setting

In the Qiongdongnan Basin (QDNB) the sedimentary succession is composed of Eocene lacustrine mudstones, Oligocene lacustrine and shallow water sediments, and Miocene deep water deposits (Zhao et al., 2015). The major source rock in this region is the over mature Yacheng Formation (type II-III), which was deposited in the Oligocene, during a period of high subsidence that promoted rapid maturation (Huang et al., 2014). It is inferred that a large quantity of liquid hydrocarbons and natural gases were generated during the mature stage from the organic matter of this source rock (Huang et al., 2014; Zhang et al., 2016). Strata deposited during the Miocene to Pliocene were in an immature - low-mature stage, and have been confirmed to be biogenic gas source rocks in the QDNB (Huang et al., 2014). Miocene deep-water deposits record another period of rapid subsidence, which started earlier in the western QDNB (≈ 10.5 Ma) than in the eastern QDNB (from 5.3 Ma). The lithology in this study area is mainly composed of hemipelagic clayey silt and/or silty clay sediment (Zhang et al., 2018). Mud diapirs, gas chimneys, and bottom simulating reflectors associated with hydrocarbon migration and gas hydrate accumulation are widely observed in the QDNB (Zhang et al., 2018).

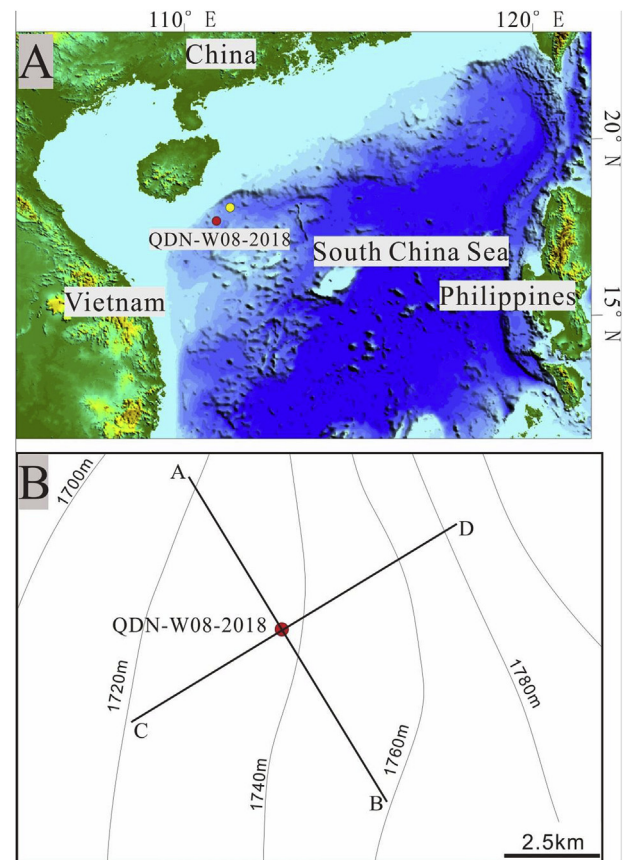


Fig. 1. A: Regional bathymetry of the northern slope of the South China Sea and the study area (from GMGS multibeam database). Red dot: QDN-W08-2018. Yellow dot: Reference site (QDN-W01-2018) of the geothermal gradient. B: Location of site QDN-W08-2018 and seismic reflection profiles AB and CD (shown in Fig. 2) on a bathymetric contour map. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3. Methodology

3.1. Seismic reflection data

In April 2018, GMGS undertook a 2D seismic reflection survey across the drilling site by R/V “FenDouSiHao” to obtain information to guide the gas hydrate drilling expedition. The vessel was equipped with a 160 cubic inch air gun array towed at depth of 3 mbsl, and shots were fired at 25 m intervals. The frequency range of the raw seismic data was 6–160 Hz with a dominant frequency of 75 Hz, and the vertical resolution is about 10 m. Seismic data were acquired with 3000 m streamers at water depth of 5 mbsl, with 6.25 m spacing between the common depth points (CDP) of measurement. To ensure full fold data acquisition, seismic records with 6 s duration were acquired with 1 ms sampling rate. The high quality seismic data were processed by the Institute of Processing in the GMGS using the GeoCluster2.1 (CGG) processing system. The seismic data were not migrated and depth conversion was not applied. The processing procedures were summarized by Wang et al. (2010).

3.2. Seafloor observations

Two ROV dives were conducted before drilling. GMGS conducted the first dive in April using the ROV “Haima”. The second dive was conducted in June using the Fugro ROV “FCV 2000D”.

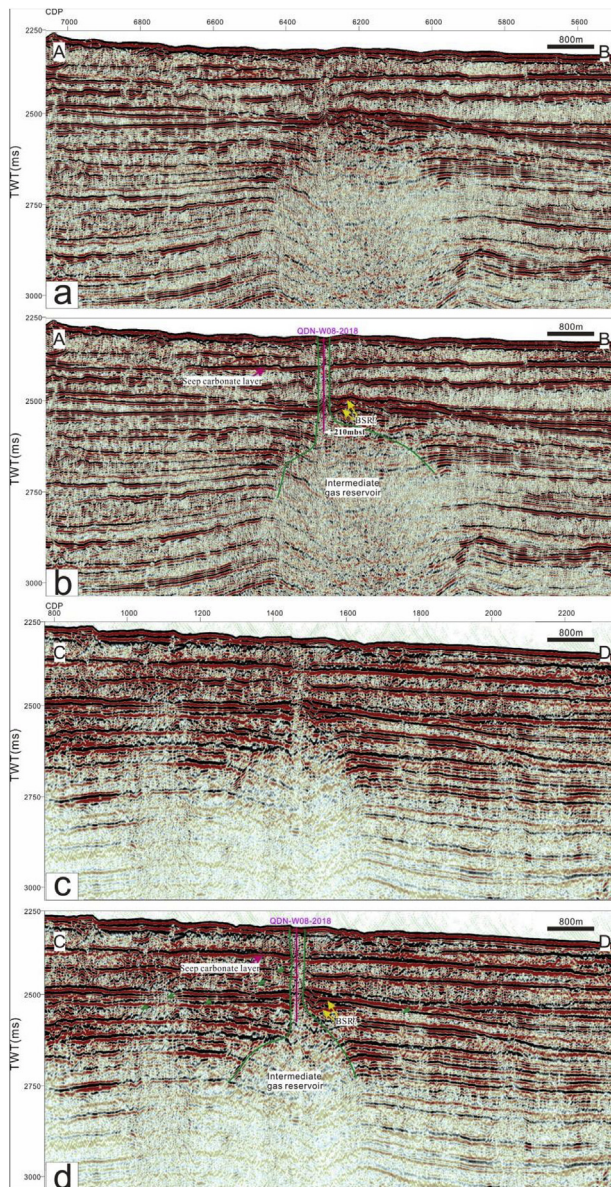


Fig. 2. Seismic reflection profiles AB and CD (locations in Fig. 1) across site QDN-W08-2018, uninterpreted in a and c, interpreted in b and d. The vertical pink lines show the borehole location. Pink and yellow arrows denote an interpreted carbonate layer (~ 4.5 km laterally extent) and BSR, respectively. The green lines outline a seismically chaotic zone of blanking, which widens from 190 m above 2600 ms to up to 2 km below (interpreted as an intermediate gas reservoir below the BSR). The green arrows indicate small-scale seismic blanking. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3. Drilling and in situ tests

Site QDN-W08-2018 was chosen to penetrate a chimney-like structure interpreted from seismic profiles (see Fig. 2). Three holes were drilled at the site, including an LWD borehole (QDN-W08-2018) to understand the gas hydrate distribution and two coring boreholes (QDN-W08B-2018 and QDN-W08C-2018) to obtain samples for sedimentological geochemical analyses. LWD measurements and core processing were undertaken by Schlumberger and GeoTek, respectively. Sediment cores were acquired using non-pressure or pressure coring tools, depending on the objective (Fig. 3). Fugro in situ cone penetration tests (CPT) were conducted to measure sediment temperature and permeability. The CPT tool (with temperature and pressure sensors)

penetrated into the sediment for 1–1.5 m and was left for 30 min to reach pressure and temperature equilibrium. Geothermal gradient was estimated by linear fit of the measured temperatures. Permeability was calculated based on the pore pressure dissipation rate. Coring and CPT tests were not continuous, and the detailed coring depths are shown in Fig. 3.

Recovered pressure cores were processed using the Pressure Core Analysis and Transfer System (PCATS), and an X-ray image with a pixel resolution of 120 μm was automatically collected using a microfocal source. Detailed information about the PCATS can be found in Priest et al. (2015).

3.4. Geochemical analyses

Pore water samples were collected from non-pressure cores on recovery, taking care to avoid contamination from seawater or drilling mud. The sediment samples were squeezed in titanium cells and the pore water obtained was analyzed by ion chromatography (Dionex ICS-2100), with a sulfate detection limit below 0.1 mM.

Void gas and hydrate-bound gas in the non-pressure cores were sampled and analyzed for composition using an Inficon Fusion MicroGC gas chromatograph with a molecular sieve and PLOT Q columns and thermal conductivity detectors. Oxygen, nitrogen, methane, ethane, propane, butane, iso-butane, iso-pentane, and pentane were measured. The detection limit for all gases was 10 ppm and the quantification limit was 30 ppm. Gas content between 10 and 30 ppm is labeled as “trace” in Table 1.

3.5. Gas hydrate distribution

The distribution of gas hydrate was interpreted from core observations and geophysical well-log measurements. Conventional cores were scanned with an infrared camera when arriving on deck to identify low temperature anomalies indicative of hydrate dissociation, which is an endothermic process (Long et al., 2004; Weinberger et al., 2005). For pressure cores, gas hydrate was identified from the P-wave velocity and electrical resistivity data as well as the X-ray CT scanning.

The vertical distribution of gas hydrates was also constrained using its stability conditions for measured gas compositions. The phase boundary of gas hydrate was calculated with CSMHYD software (Sloan Jr and Koh, 2007). Using data of gas composition, seafloor temperature and geothermal gradient, and by assuming porewater salinity of 3.5% NaCl solution, the bottom and top boundaries of the gas hydrate stability zone were estimated.

4. Results

4.1. ROV observations of the drilling site

The water depth of the ROV survey area (drill site QDN-W08-2018) is approximately 1740 m (Fig. 1). No significant changes were observed on the greyish seafloor between two dives conducted in April and June (Fig. 4A–D). A dome-like structure (3–5 m high and 6–10 m root diameter) was observed prior to the drilling expedition (Fig. 4C). Typical elements characterizing cold seep environments, such as seep-associated bivalve fragments (Fig. 4A–D) and tube worms (Fig. 4D), were scattered on the periphery of the dome. The length of the bivalve shell was about 10–20 cm and the diameter of the bivalve fragment clusters was up to several meters. Gas emissions were not observed during the ROV dives prior to drilling.

4.2. Seismic observations

The QDN-W08-2018 drilling site is located within a vertical structure observed on seismic profiles, interpreted to be the upper part of a gas chimney (Fig. 2). The seismic profiles show complex seafloor

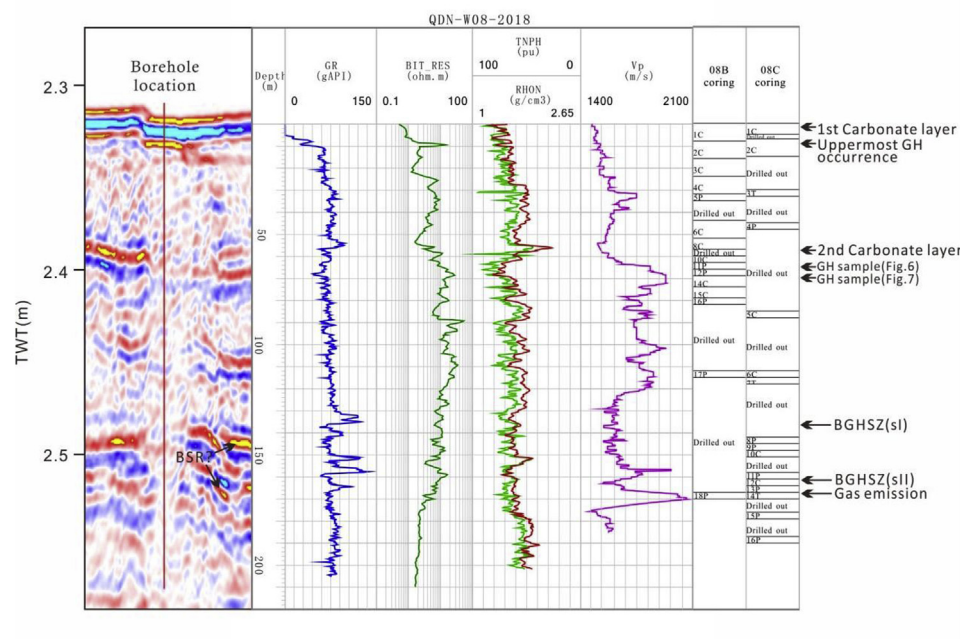


Fig. 3. At left: detail of seismic profile across drill site; to right: geophysical LWD data (GR: Gamma Ray. BIT_RES: Bit Resistivity. TNPH: Thermal Neutron Porosity. RHON: Bulk Density from Neutron. Vp: P-wave Velocity) from QDN-W08-2018. BGHSZ(sI) and BGHSZ(sII) represent the calculated base of gas hydrate stability zone for sI methane hydrate and sII gas hydrate (10% C₂H₆). The two right-hand columns show the cored intervals in O8B and O8C ('drilled out' indicates no core recovery). Gas emission was observed by the camera on the seabed frame when the drill bit reached 167 mbsf C: non pressure core. P: pressure core. T: CPT test.

features around the drilling site, such as domes (Fig. 2). In the sub-surface, the chimney is a vertical column of chaotic reflections about 190 m wide, which widens below about 2600 ms (~190 mbsf) to form a blanking zone of faint chaotic or dipping reflections up to 2000 m wide (Fig. 2). A high amplitude reflector of negative polarity at 165 mbsf, laterally extends to either side of the chimney, is inferred to be the local BSR (bottom simulating reflector). The seismic blanking observed in and below the chimney (Fig. 2), is interpreted to represent gas migration along fractures or small-scale faults. This interpretation is supported by dipping-reflections below the BSR that are interpreted as pull-down effects rather than stratal deformation (Zhang et al., 2018).

4.3. Geothermal gradient and permeability

In situ temperature and permeability were measured at seven depths in boreholes QDN-W08B-2018 and QDN-W08C-2018 as shown in Table 2. The temperatures give a linear geothermal gradient of 102 °C/km (Table 2, Fig. 5A). The regional geothermal gradient was estimated at a reference site QDN-W01-2018, which is located 50 km northeast of the site QDN-W08-2018 (Fig. 1). The reference site is not thought to be affected by vertical fluid migration, and yields a gradient of approximately 65 °C/km (Table 2). This reference gradient is significantly lower than that from the chimney structure at site QDN-W08C-2018. The measured permeability at different depths (see Table 2) of QDN-W08B-2018 and QDN-W08C-2018 ranges from 1 mD to 64 mD.

Table 1

Gas composition of void gas and hydrate-bound gas.

Borehole	Depth (mbsf)	Sample type	C1 (%)	C2 (%)	C3 (%)	i-C4 (ppm)	n-C4 (ppm)	i-C5 (ppm)	n-C5 (ppm)	CO2 (ppm)	C1/(C2 + C3) Molar ratio
QDN-W08B	27.52	void gas	94.2	4.5	0.74	1784	704	220	b.d.	n.a.	18
QDN-W08C	87.35	void gas	92.2	5.3	1.65	4086	1533	619	trace	1852	13
QDN-W08C	89.66	void gas	90.5	6.3	2.24	5487	1612	443	trace	1378	11
QDN-W08C	90.23	void gas	89.9	6.5	2.45	6076	1891	612	trace	1932	10
QDN-W08C	113.00	void gas	93.2	4.8	1.41	3342	1263	338	trace	7678	15
QDN-W08C	142.39	void gas	87.4	9.3	1.94	4541	1503	1125	trace	4767	8
QDN-W08C	143.99	void gas	89.6	7.8	1.52	3617	1380	1168	trace	1478	10
QDN-W08C	150.02	void gas	91.8	n.a.	6.37	14833	2488	120	b.d.	1254	n.a.
QDN-W08C	150.88	void gas	91.2	n.a.	6.87	16118	2407	121	b.d.	910	n.a.
QDN-W08C	151.54	void gas	91.1	n.a.	6.91	16219	2352	119	b.d.	558	n.a.
QDN-W08C	164.49	void gas	70.1	17.6	9.88	20618	1807	187	trace	3363	3
QDN-W08C	165.28	void gas	74.3	16.4	7.49	15428	1860	352	trace	1687	3
QDN-W08B	53.02	hydrate	98.4	1.3	0.18	441	516	trace	40	5231	69
QDN-W08B	53.02	hydrate	97.8	1.4	0.46	1130	574	41	b.d.	n.a.	54
QDN-W08B	53.68	hydrate	98.1	0.2	1.27	b.d.	3633	b.d.	152	17141	68
QDN-W08B	62.93	hydrate	82.2	11.0	4.75	11342	8460	39	65	2727	5
QDN-W08B	65.10	hydrate	97.4	2.3	0.09	280	125	87	b.d.	6534	40
QDN-W08B	81.71	hydrate	85.5	9.8	3.54	8976	1978	189	27	n.a.	6
QDN-W08C	8.00	hydrate	97.5	2.2	0.05	123	85	68	trace	9877	43
QDN-W08C	85.00	hydrate	98.2	1.2	0.26	691	1392	580	trace	9663	68
QDN-W08C	145.37	hydrate	92.1	n.a.	6.26	13838	2413	53	b.d.	3340	n.a.
QDN-W08C	145.37	hydrate	92.3	n.a.	6.14	13192	2183	49	trace	3953	n.a.

b.d: below detection. n.a: not analyzed.

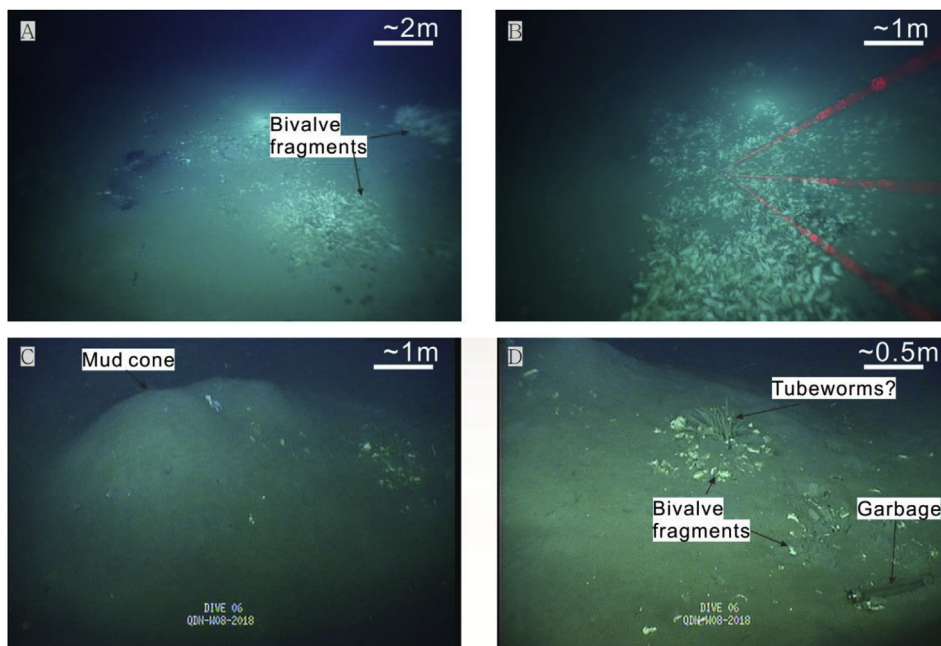


Fig. 4. ROV seafloor observations at site QDN-W08-2018 prior to drilling. A and B are seafloor photos obtained by GMGS ROV “HaiMa” in April 2018. C and D are seafloor photos obtained by Fugro ROV “FCV 2000D” in June 2018. The red light beams are the laser beams used to estimate the distance (10 cm apart). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2

In situ temperature measured in boreholes 08B and 08C (along with permeability) and at reference borehole W01B.

Borehole	Test NO.	Sensor depth (mbsf)	Permeability (mD)	Temperature (°C)	Geothermal Gradient (°C/km)
QDN-W08B-2018	CPT01*	–	–	–	102
	CPT02	69.6	64	10.5	
QDN-W08C-2018	CPT01	31.6	2	6.4	
	CPT02	116.4	4	15.3	
	CPT02	118	5	15.5	
	CPT03	168.5	2	19.8	
	CPT03	170	1	21	
QDN-W01B-2018	CPT01	58.4	–	6.3	65
	CPT01	59.8	–	6.6	
	CPT02	159.5	–	13.2	
	CPT02	160.9	–	13.3	
	CPT03	253	–	18.8	
	CPT03	254.4	–	19.2	

Note: Same Test NO indicates the one deployment with two penetrations.

4.4. Pore water chemistry

Pore water sulfate concentrations are ≈ 28 mM at the seafloor but decrease to 0 mM in all pore water samples below the first sample at 0.4 mbsf (Fig. 6A). The sulfate reduction methane oxidation interface is inferred to be shallower than 0.4 mbsf, indicating an upward gas flux at the drilling site. The chloride concentration of bottom water in the study area is around 550 mM. Chloride concentrations in pore waters are ~ 310 mM at 0.4 mbsf and shows anomalies of up to ~ 640 mM between 12 mbsf and 55 mbsf, and below 55 mbsf, decrease to ~ 150 mM (Fig. 6B). The high chloride anomalies (12–55 mbsf) may suggest active hydrate formation near the seafloor because hydrate formation is related to ion exclusion process (Torres et al., 2004, 2011b). The low chloride anomalies (> 55 mbsf) are caused by fresh water released from gas hydrate dissociation during core retrieval (Torres et al., 2011a).

4.5. Gas hydrate distribution and morphology

Gas hydrates were recovered from various depths (9–151 mbsf) where LWD data show high resistivity anomalies of up to 73Ω m between (9–174 mbsf) (Fig. 3). Small depth discrepancies between coring

and LWD are inferred to result from the non-continuous coring and core recovery. The gamma ray shows high anomaly spikes at 54.6 mbsf (increasing from 75 to 90 gAPI) and at 131–167 mbsf (maximum = 136 gAPI), respectively (Fig. 3). The deeper gamma ray anomaly corresponds to the high amplitude reflector interpreted as a BSR (Fig. 2). P-wave velocities range between 1465 and 2060 m/s and is higher than 1600 m/s in most intervals between 30 and 174 mbsf, with the highest value of 2046 m/s at 170 mbsf. Gas emission was observed by the camera on the seabed frame when the drill bit reached 167 mbsf.

Gas hydrate samples of different size and morphology were recovered from various depths. Fig. 7 shows gas hydrate veins with different dipping angles and thickness identified by X-ray scanning of the pressure cores (63–65.3 mbsf). Massive gas hydrate nodules up to 50 cm thick were recovered from 69 mbsf (Fig. 8).

4.6. Gas compositions

Methane is the dominant constituent (70.1–98.3%) of both void gas and hydrate-bound gas samples (Fig. 9A). Besides methane, CO_2 (< 0.001 –1.71%) and other higher order hydrocarbons were also detected, including C_2H_6 (0.16–17.59%), C_3H_8 (0.05–9.88%), $i\text{-C}_4\text{H}_{10}$ (< 0.001 –2.06%), $n\text{-C}_4\text{H}_{10}$ (< 0.001 –0.85%), $i\text{-C}_5\text{H}_{12}$

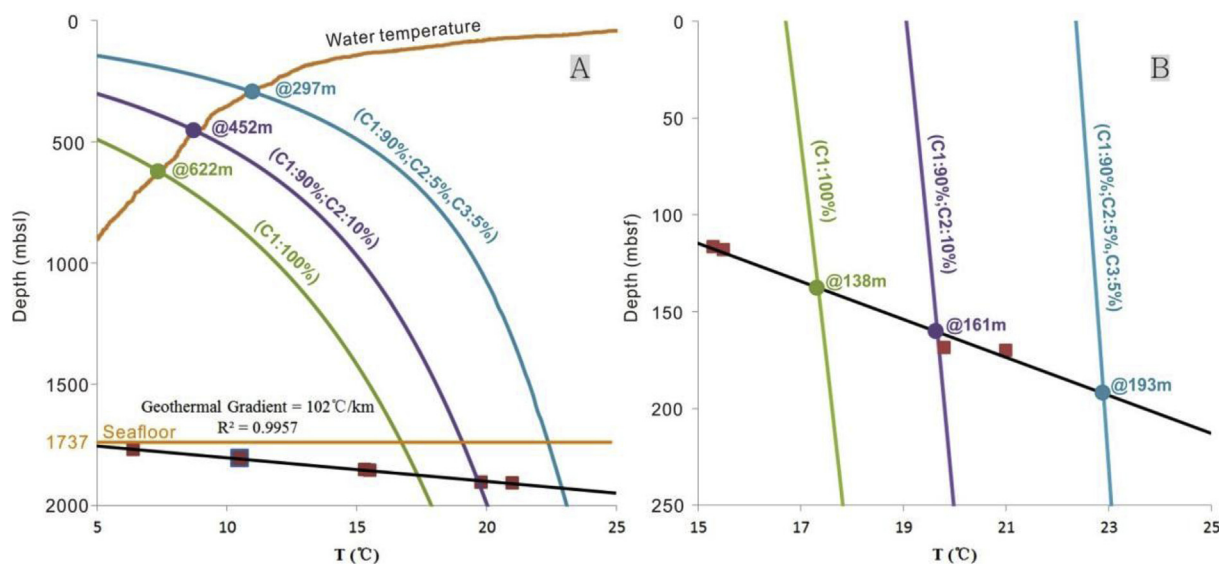


Fig. 5. A: Phase boundaries for sI hydrate (100% methane) and sII hydrate (C1:C2 = 9:1; C1:C2:C3 = 9:0.5:0.5) were calculated using CSMHYD software (Sloan Jr and Koh, 2007). The water temperature is from the CTD test during GMGS5. The seafloor depth of the drillsite is shown together with in situ temperature measurements made at site QDN-W08-2018 (see Table 2). B: detail of A.

(< 0.001–0.12%), n-C₅H₁₂ (< 0.001–0.02%) (Fig. 9B–F, Table 1). The C₁/(C₂ + C₃) ratio is 3–69. With increasing sediment depth, gas content shows a general decrease in methane and increase in C₂ + gases.

The presence of C₂ + hydrocarbons indicates the occurrence of sII or sH gas hydrates. In order to understand their possible occurrence, we calculated the gas hydrate stability zone for three different scenarios (sI methane hydrate; sII gas hydrate with 10% ethane; sII gas hydrate with 5% ethane and 5% propane). The result shows that if the gas hydrate at the drilling site is sI methane hydrate, the BGHSZ is estimated to be at ~138 mbsf (Fig. 6B). However, gas hydrate samples were recovered down to 158 mbsf, consistent with the occurrence of sII or sH gas hydrates. Therefore, sII/sH gas hydrates are inferred to occur at this gas

chimney site, as supported by geochemical data (Fig. 9).

4.7. Buried authigenic carbonates

Authigenic carbonates of different thickness (~ cm to ~ dm) were recovered from the seafloor and from sediment depths of ~3 mbsf, ~52.1 mbsf and ~53.6 mbsf at QDN-W08B-2018 (Fig. 8A–D). Whole round hard carbonate rocks, which are mainly grey and yellow, were sampled in the liners at 52.1 mbsf and 53.6 mbsf. Interconnected pores and fractures can be observed in the carbonates. Shallow carbonate rocks recovered at 3mbsf were not as stiff as the deep ones and were broken into pieces during drilling. Typical seep-related bivalve

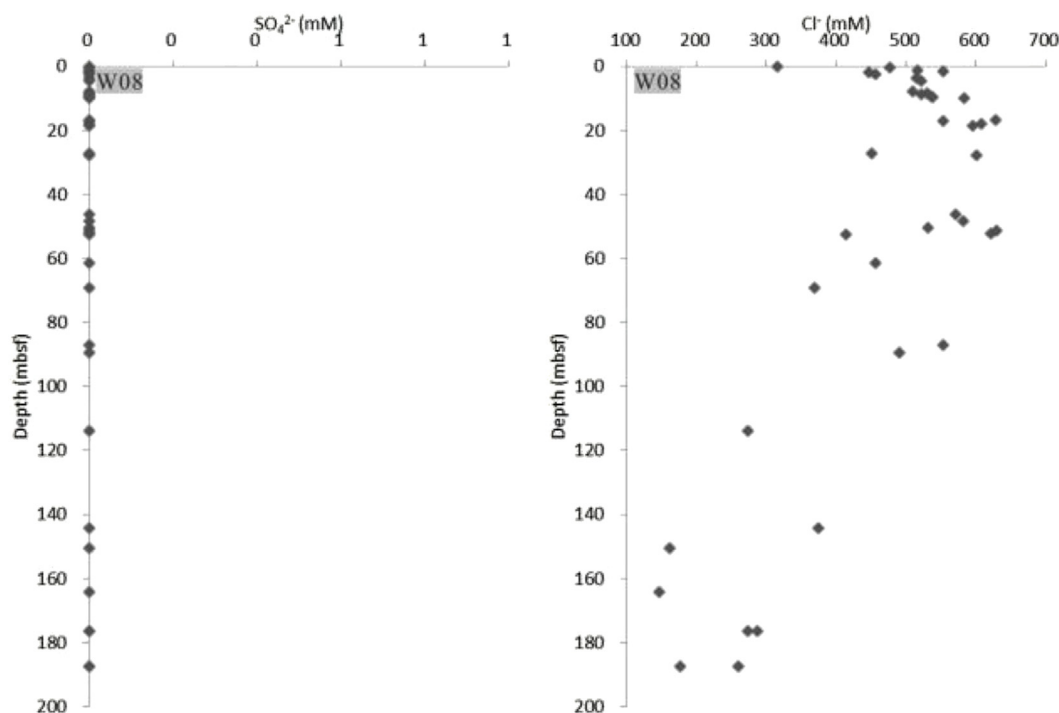


Fig. 6. Pore water sulfate and chloride concentration profiles of drill site QDN-W08-2018.

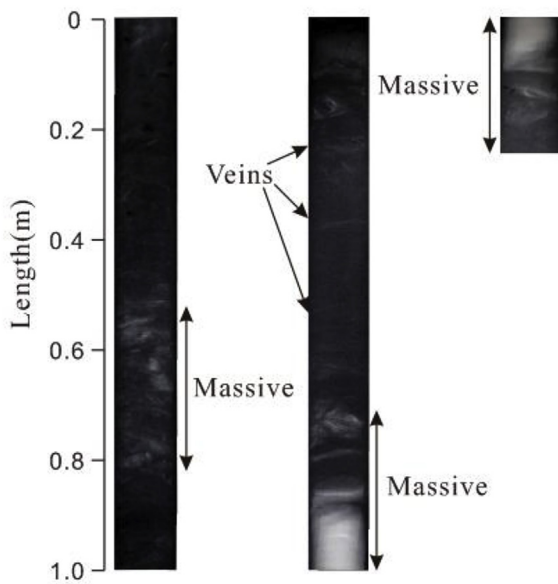


Fig. 7. X-ray image of pressure core 11P (See Fig. 3) of QDN-W08B-2018 (63–65.3 mbsf). Light color is massive gas hydrate and veins, dark colors are sediment.

fragments and mud were cemented in the carbonates (Fig. 8C and D). Gas hydrate pieces were observed within the porous carbonate rocks in a non-pressure core at 52.1 mbsf (Fig. 8B). The carbonates recovered from 52.1 to 53.6 mbsf coincide with a peak in density values of up to 2.2 g/cm^3 between 52 and 54 mbsf (Fig. 3). The LWD density peak and carbonated samples coincide with a strong positive amplitude reflection in the seismic profile at ~ 54 mbsf which laterally extends ~ 4500 m through the drill site (Fig. 2).

5. Discussion

5.1. Complex gas hydrate within a gas chimney

Gas hydrate-bearing sediments exhibit high resistivity and high P-wave velocity compared to the non-hydrate bearing sediments (Collett et al., 2012). The presence of free gas can also increase resistivity; however, free gas in sediments significantly decreases the P-wave velocity of the sediment (Lee, 2004). LWD profiles from QDN-W08B-2018 show fluctuating resistivity and P-wave velocities, which we infer to reflect the presence of free gas within hydrate-bearing sediments between 9 and 174 mbsf.

C2+ hydrocarbons may result in the formation of sII and sH gas hydrate (Sloan, 2003). sI and sII gas hydrates have been discovered independently in marine sediments in several areas (Hester et al., 2007; Klapp et al., 2010; Lu et al., 2005; Murshed et al., 2008), whereas sH gas hydrate has only been reported in the Gulf of Mexico (Sassen and Macdonald, 1994) and on the continental slope of Canada (Lu et al., 2007). In addition, sH gas hydrates has been inferred offshore NE Borneo from the detection of C₄+ gases within the hydrate stability zone (Paganoni et al., 2016). The presence of pentane up to 0.015% (Table 1) in this study indicates the potential minor occurrence of sH hydrate (Lu et al., 2007). In addition, the gas composition profiles (Fig. 8) indicate a relative enrichment in methane towards shallower depths. This trend may indicate a transition from dominant sII/H hydrates to dominant sI hydrates (from the gas chimney roots towards the gas chimney top, Fig. 10). Further investigations on gas hydrate samples, including Raman spectroscopy and X-ray diffraction analyses, are necessary to confirm the presence of sII/sH hydrate at the drill site.

The BGHSZ of sII gas hydrate (10% ethane) lies at 161 mbsf, which is between 158 mbsf and 167 mbsf (interpreted source depth of the drilling-induced gas emission). The thickness of sII GHSZ (10% ethane) is 15% higher than that of sI GHSZ. The BGHSZ of sII gas hydrate is estimated to lie at 193 mbsf for a composition including 5% ethane and 5% propane. The drill site did not reach this depth, but the void gas at ~ 167 mbsf contains more than 5% ethane and propane, indicating the potential co-existence of gas and gas hydrates below 167 mbsf. It is inferred that the low permeable hydrate-bearing sediment is

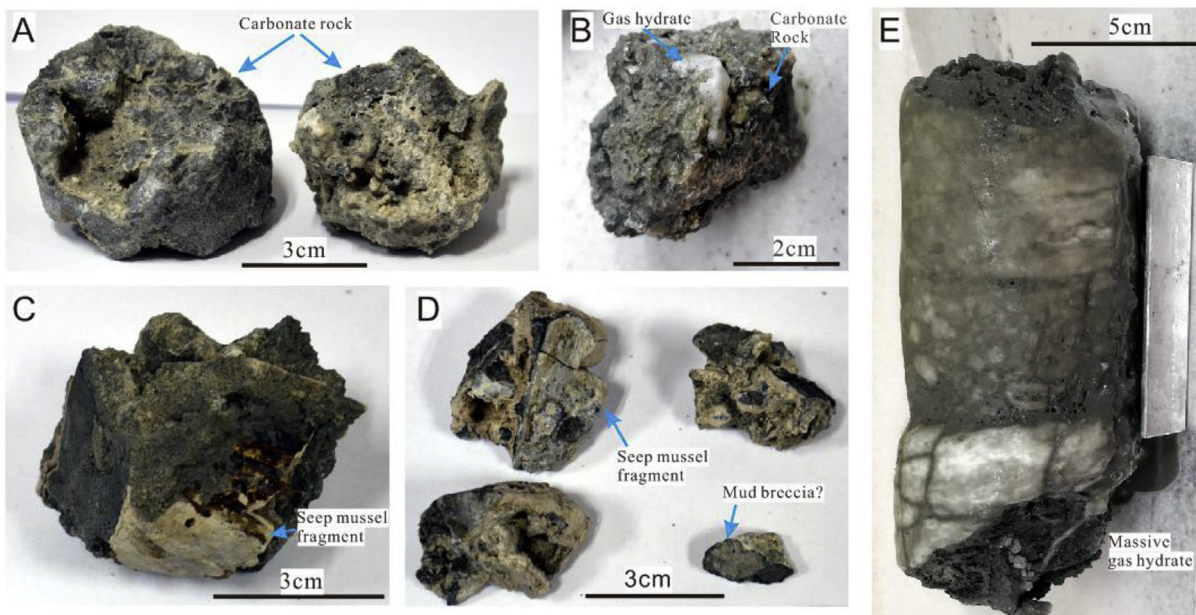


Fig. 8. Photos of carbonate samples (A–D) and massive gas hydrate (E) recovered from different depths in QDN-W08-2018. A&B: Whole round carbonate rocks recovered at 53.6 mbsf. C&D: Carbonate rocks with bivalve fragments recovered at 3 mbsf and 52.1 mbsf, respectively. E: Whole round massive gas hydrate recovered at 69 mbsf.

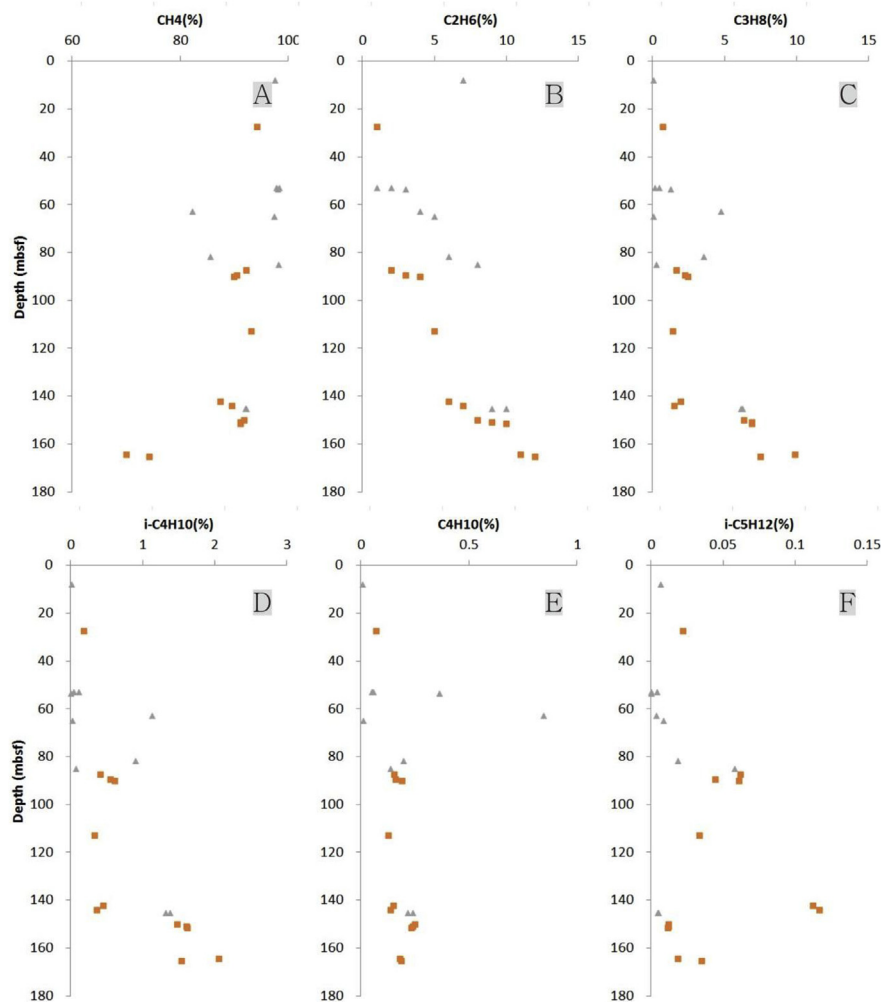


Fig. 9. Gas compositions determined from samples of void gas (rectangles) and hydrate-bound gas (triangles). See also Table 1.

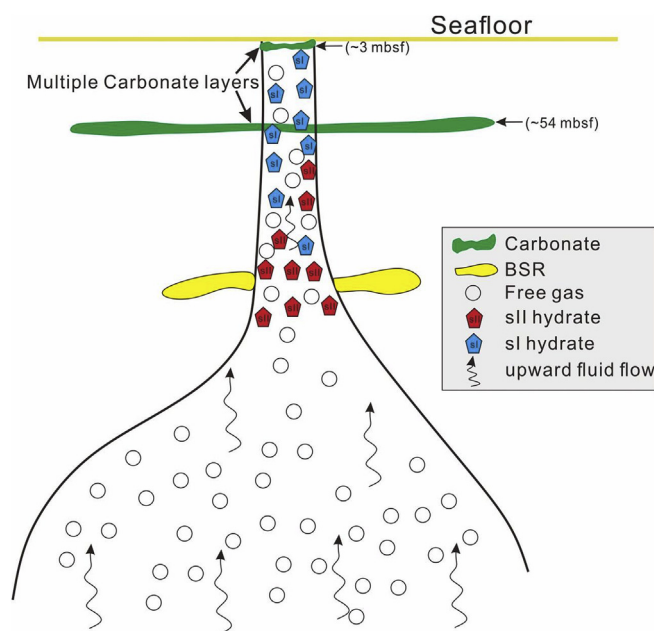


Fig. 10. Schematic model of the complex gas hydrate system within the gas chimney driven by upward migration of thermogenic and biogenic gas, as well as evidence of the paleo cold seep activity.

responsible for blocking the migration pathways and contact with free water, leading to gas accumulation beneath 167 mbsf.

The global amount of hydrate-bound carbon, which is mainly estimated based on the assumption that natural gas hydrate is sI methane hydrate (Burwicz et al., 2011; Pinero et al., 2013), might be underestimated because sII hydrate has a larger stability zone (Paganoni et al., 2016; Plaza-Faverola et al., 2017; Qian et al., 2018; Sassen et al., 2013). It should also be noted that more energy is needed to dissociate sII hydrate than sI hydrate; therefore, serious consideration should be given to designing a production technique for sII gas hydrate.

The top of sII GHSZ (10% ethane) is estimated to lie at 497 mbsl, about 125 m shallower than that of sI hydrate (Fig. 5A and B). As a result, the life time of gas bubbles with significant C_2+ hydrocarbons in the water column will be longer with sII hydrate coat than with sI hydrate coat (Leifer et al., 2015; Rehder et al., 2002). This means that the existence of sII hydrate increases the possibility of gas bubbles entering the upper water column or even into the atmosphere (Wei et al., 2018).

5.2. Fluid sources and migration pathways

Both the void and hydrate-bound gas contain heavier (C_2+) hydrocarbons, indicating a thermogenic source in the deep subsurface. A smell of oil in some sediment portions when opening the cores also supports the existence of a deep petroleum system (Milkov et al., 2005). Previous studies have distinguished source rocks at three levels within the Miocene to Pliocene succession, which might provide biogenic gas

for the formation of gas hydrate (Wang et al., 2010). However, this is not supported by the thermogenic gas inferred in this study. Therefore, it is inferred that our gas hydrate system is sourced by Oligocene source rock which generated thermogenic hydrocarbons (Huang et al., 2014). Several processes are suspected to be involved during fluid migration from the source rocks to the gas hydrate reservoir. The blanking zone beneath the BSR is interpreted as an intermediate gas reservoir, which is suspected to serve as the intermediate gas storage between the gas hydrate system and the source rocks. It is unclear from the seismic data how gas has migrated from the source rock to the intermediate gas reservoir. However, the gas chimney is suggested to act as a major pathway for fluid migration from the intermediate gas reservoir to shallow sediment above the BSR. The seafloor gas emission observed when the drill bit reached 167 mbsf (Fig. 3) indicates that the gas reservoir stores free gas and provides sufficient fluid to support the occurrence of free gas and gas hydrate in the gas chimney. Intermediate gas storage and expulsion have been reported from many sites, including offshore Norway (Hustoft et al., 2010; Plaza-Faverola et al., 2011), NW Borneo (Paganoni et al., 2017), the Arctic (Andreassen et al., 2017), the Gulf of Mexico (Solomon et al., 2008) and Hydrate Ridge (Bangs et al., 2011a).

Gas hydrate decreases the permeability of the sediment, therefore inhibiting upward migration of fluids above the base of the gas hydrate stability zone (Wei et al., 2015). The low permeability recovered in the drill site (1–5 mD, see Table 2) is capable of causing pressure build-up and hydro-fracture, as opposed to capillary invasion through the pore space (Sultan et al., 2014). The high observed geothermal gradient (102 °C/km) supports vertical advection of warm fluids and potentially hydrocarbons (Wei et al., 2015; Wu et al., 2019). The seismic blank zone narrows above 190 mbsf, indicating that fluid migration is vertically focused along the gas chimney which potentially contains shallow fractures and faults. Upward within the chimney, methane content increases while other heavier hydrocarbons decrease, probably being resulted from the molecular/compositional fractionation during gas migration, or mixing with shallow biogenic gas and/or degradation of the thermogenic gas (Kida et al., 2006; Paganoni et al., 2016; Pape et al., 2010; Sassen et al., 1999; Sassen et al., 2001; Smith et al., 2014). Future stable carbon isotopic analysis of both methane and C₂ + hydrocarbons will be conducted to help in distinguishing the major processes. The interconnected pores and fractures in the carbonate layers (Fig. 8B), which were previously occupied by organisms, provide not only efficient fluid pathways but also the accommodation space for gas hydrates.

5.3. Cold seep activity in the past

Seep-related bivalves can only live on the seafloor (Levin, 2005). The well-preserved bivalve fragments recovered in authigenic carbonates at 3 mbsf and 52.1 mbsf (Fig. 8C&D) are inferred to have formed in the past. Carbonates recovered at multiple levels within the drilled sediment succession, indicate seepage at different time periods. The age of past cold seep activity can be estimated based on the local sedimentation rate. Sediments in the study area are mainly sourced from rivers and gravity driven flows at a sedimentation rate of ~1 m/ka as suggested by previous petroleum drilling data (Wei et al., 2018; Wang et al., 2010b). This suggests that authigenic carbonate concretions at 3 mbsf and 52.1 mbsf formed during seepage at ~3 ka and 0.52–0.54 Ma, respectively.

The authigenic carbonate sample at 52.1 mbsf coincides with a high-amplitude reflector at ~54 mbsf that extends laterally over 4500 m (see Fig. 2), which we interpret to indicate the carbonate concretions were developed not only within the gas chimney but across the paleo-seafloor. We infer that such widespread ancient cold seep activity was not controlled by the present gas chimney, but by other factors of broader spatial influence such as low fluid flux activity along fractures (Fig. 10). The recurrent activity of the cold seep may have

been triggered either by overpressure within the deep reservoirs (Bangs et al., 2011b) or by gas hydrate dissociation potentially associated with sea level change, bottom water temperature variation, sedimentation rate and tectonic uplifting (Berndt et al., 2014). However, further information on the age of the sediments and carbonate rocks is necessary to accurately date the paleo cold seeps and to further discuss possible trigger mechanisms.

6. Conclusions

Based on the analysis of multidisciplinary data obtained by drilling into a chimney structure in the QingDongNan sea area of the South China Sea, including LWD data and coring information, a complex gas hydrate system is identified. Gas hydrates co-exist with free gas between 9 and 174 mbsf based on coring results and LWD resistivity and P-wave velocity logs. High chloride anomalies in sediment pore waters near seafloor (12–55mbsf) indicate ongoing gas hydrate formation. Heavier hydrocarbons (C₂+) indicate the gas is thermogenic and probably experienced fractionation or admixture with biogenic gas and/or degradation during migration from a deep source. The gas chimney is interpreted to facilitate gas migration from an intermediate gas reservoir below a local BSR to form gas hydrate in shallow sediment within the GHSZ. The presence of heavier hydrocarbons and gas hydrate occurrence below the sl BGHSZ indicates that slI hydrate (possibly also sH) exists in this complex gas hydrate system. This means that the stability zone is thicker than for methane hydrates, increasing the size of the gas hydrate reservoir. Authigenic carbonate concretions recovered from two main levels (3 mbsf and 52.1–53.6 mbsf) indicate that the cold seeps have been recurrently active over timescales of up to 0.54 Ma. The deeper layer coincides with a laterally extensive strong seismic reflector that may indicate an episode of widespread rather than focused fluid migration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpetgeo.2019.03.023>.

References

- Abegg, F., Hohnberg, H.-J., Pape, T., Bohrmann, G., Freitag, J., 2008. Development and application of pressure-core-sampling systems for the investigation of gas-and gas-hydrate-bearing sediments: deep Sea Research Part I. *Oceanographic Research Papers* 55 (11), 1590–1599.
- Andreassen, K., Hubbard, A., Winsborrow, M., Patton, H., Vadakkepuliambatta, S., Plaza-Faverola, A., Gudlaugsson, E., Serov, P., Deryabin, A., Mattingsdal, R., 2017. Massive blow-out craters formed by hydrate-controlled methane expulsion from the Arctic seafloor. *Science* 356 (6341), 948–953.
- Bangs, N.L., Hornbach, M.J., Berndt, C., 2011a. The mechanics of intermittent methane venting at South Hydrate Ridge inferred from 4D seismic surveying. *Earth Planet. Sci. Lett.* 310 (1), 105–112.
- Bangs, N.L., Hornbach, M.J., Berndt, C., 2011b. The mechanics of intermittent methane venting at South Hydrate Ridge inferred from 4D seismic surveying. *Earth Planet. Sci. Lett.* 310 (1–2), 105–112.
- Bayon, G., Dupré, S., Ponzevara, E., Etoubleau, J., Chéron, S., Pierre, C., Mascle, J., Boetius, A., De Lange, G.J., 2013. Formation of carbonate chimneys in the Mediterranean Sea linked to deep-water oxygen depletion. *Nat. Geosci.* 6 (9), 755.
- Berndt, C., Feseker, T., Treude, T., Krastel, S., Liebetrau, V., Niemann, H., Bertics, V.J., Dumke, I., Dünnbier, K., Ferré, B., Graves, C., Gross, F., Hissmann, K., Hühnerbach,

- V., Krause, S., Lieser, K., Schauer, J., Steinle, L., 2014. Temporal constraints on hydrate-controlled methane seepage off svalbard. *Science* 343 (6168), 284–287.
- Blinova, V., Ivanov, M., Bohrmann, G., 2003. Hydrocarbon gases in deposits from mud volcanoes in the Sorokin Trough, north-eastern Black Sea. *Geo Mar. Lett.* 23 (3–4), 250–257.
- Blumenberg, M., Walliser, E.-O., Taviani, M., Seifert, R., Reitner, J., 2015. Authigenic carbonate formation and its impact on the biomarker inventory at hydrocarbon seeps—a case study from the Holocene Black Sea and the Plio-Pleistocene Northern Apennines (Italy). *Mar. Petrol. Geol.* 66, 532–541.
- Bohrmann, G., Greinert, J., Suess, E., Torres, M., 1998. Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability. *Geology* 26 (7), 647–650.
- Burwicz, E.B., Rüpke, L., Wallmann, K., 2011. Estimation of the global amount of submarine gas hydrates formed via microbial methane formation based on numerical reaction-transport modeling and a novel parameterization of Holocene sedimentation. *Geochim. Cosmochim. Acta* 75 (16), 4562–4576.
- Collett, T.S., Lee, M.W., Zyryanova, M.V., Mrozewski, S.A., Guerin, G., Cook, A.E., Goldberg, D.S., 2012. Gulf of Mexico gas hydrate joint industry Project leg II logging-while-drilling data acquisition and analysis. *Mar. Petrol. Geol.* 34 (1), 41–61.
- Cook, A.E., Goldberg, D., Kleinberg, R.L., 2008. Fracture-controlled gas hydrate systems in the northern Gulf of Mexico. *Mar. Petrol. Geol.* 25 (9), 932–941.
- Dickens, G.R., 2003. Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor. *Earth Planet. Sci. Lett.* 213 (3–4), 169–183.
- Feng, D., Birgel, D., Peckmann, J., Roberts, H.H., Joye, S.B., Sassen, R., Liu, X.-L., Hinrichs, K.-U., Chen, D., 2014. Time integrated variation of sources of fluids and seepage dynamics archived in authigenic carbonates from Gulf of Mexico Gas Hydrate Seafloor Observatory. *Chem. Geol.* 385, 129–139.
- Han, X., Suess, E., Liebetrau, V., Eisenhauer, A., Huang, Y., 2014. Past methane release events and environmental conditions at the upper continental slope of the South China Sea: constraints by seep carbonates. *Int. J. Earth Sci.* 103 (7), 1873–1887.
- Hester, K.C., Dunk, R.M., White, S.N., Brewer, P.G., Peltzer, E.T., Sloan, E.D., 2007. Gas hydrate measurements at Hydrate Ridge using Raman spectroscopy. *Geochim. Cosmochim. Acta* 71 (12), 2947–2959.
- Huang, B., Wang, Z., Gang, L., 2014. Natural Gas Source and Migration-Accumulation Pattern in the Central Canyon, the Deep Water area, Qiongdongnan Basin: China Offshore Oil & Gas.
- Hustoft, S., Bünnz, S., Mienert, J., 2010. Three-dimensional seismic analysis of the morphology and spatial distribution of chimneys beneath the Nyegga pockmark field, offshore mid-Norway: Basin Res. 22 (4), 465–480.
- Iii, G.W.L., Rozan, T.F., Taillefer, M., Nuzzio, D.B., Meo, C.D., Shank, T.M., Lutz, R.A., Cary, S.C., 2001. Chemical speciation drives hydrothermal vent ecology. *Nature* 410 (6830), 813–816.
- Kida, M., Khlystov, O., Zemskaya, T., Takahashi, N., Minami, H., Sakagami, H., Krylov, A., Hachikubo, A., Yamashita, S., Shoji, H., Poort, J., Naudts, L., 2006. Coexistence of structure I and II gas hydrates in Lake Baikal suggesting gas sources from microbial and thermogenic origin. *Geophys. Res. Lett.* 33 (24), L24603.
- Klapp, S.A., Murshed, M.M., Pape, T., Klein, H., Bohrmann, G., Brewer, P.G., Kuhs, W.F., 2010. Mixed gas hydrate structures at the Chapopote Knoll, southern Gulf of Mexico. *Earth Planet. Sci. Lett.* 299 (1), 207–217.
- Kvenvolden, K.A., Ginsburg, G.D., Soloviev, V.A., 1993. Worldwide distribution of sub-aquatic gas hydrates. *Geo Mar. Lett.* 13 (1), 32–40.
- Lee, M.W., 2004. Elastic velocities of partially gas-saturated unconsolidated sediments. *Mar. Petrol. Geol.* 21 (6), 641–650.
- Leifer, I., Solomon, E., von Deimling, J.S., Rehder, G., Coffin, R., Linke, P., 2015. The fate of bubbles in a large, intense bubble megaplume for stratified and unstratified water: numerical simulations of 22/4b expedition field data. *Mar. Petrol. Geol.* 68, 806–823.
- Levin, L.A., 2005. Ecology of Cold Seep Sediments: Interactions of Fauna with Flow, Chemistry and Microbes, Oceanography and Marine Biology. CRC Press, pp. 11–56.
- Li, N., Yang, X., Peng, J., Zhou, Q., Chen, D., 2018. Paleo-cold seep activity in the southern South China Sea: evidence from the geochemical and geophysical records of sediments. *J. Asian Earth Sci.* 168, 106–111.
- Li, J., Ye, J., Qin, X., Qiu, H., Wu, N., Lu, H., Xie, W., Lu, J., Peng, F., Xu, Z., Lu, C., Kuang, Z., Wei, J., Liang, Q., Lu, H., Kou, B., 2018. The first offshore natural gas hydrate production test in South China Sea. *China Geology* 1 (1), 5–16.
- Liu, C., Ye, Y., Meng, Q., He, X., Lu, H., Zhang, J., Liu, J., 2012. The characteristics of gas hydrates recovered from Shenhu area in the South China sea. *Mar. Geol.* 307–310 (0), 22–27.
- Liu, C., Meng, Q., He, X., Li, C., Ye, Y., Zhang, G., Liang, J., 2015. Characterization of natural gas hydrate recovered from Pearl River Mouth Basin in South China sea. *Mar. Petrol. Geol.* 61, 14–21.
- Long, P., Ussler III, W., Weinberger, J., Riedel, M., Tréhu, A., 2004. Quantification of gas hydrate abundance from infrared imaging of sub-seafloor cores. In: Proceedings AAPG Hedberg Conference.
- Lloyd, S., Sample, J., Tripathi, R., Defliese, W., Brooks, K., Hovland, M., Torres, M., Marlow, J., Hancock, L., Martin, R., 2016. Methane seep carbonates yield clumped isotope signatures out of equilibrium with formation temperatures. *Nat. Commun.* 7, 12274.
- Lu, H., Moudrakovski, I., Riedel, M., Spence, G., Dutrisac, R., Ripmeester, J., Wright, F., Dallimore, S., 2005. Occurrence and structural characterization of gas hydrates associated with a cold vent field, offshore Vancouver Island. *J. Geophys. Res.: Solid Earth* 110 (B10), B10204.
- Lu, H., Seo, Y.-t., Lee, J.-w., Moudrakovski, I., Ripmeester, J.A., Chapman, N.R., Coffin, R.B., Gardner, G., Pohlman, J., 2007. Complex gas hydrate from the Cascadia margin. *Nature* 445 (7125), 303–306.
- Milkov, A.V., Claypool, G.E., Lee, Y.-J., Sassen, R., 2005. Gas hydrate systems at Hydrate Ridge offshore Oregon inferred from molecular and isotopic properties of hydrate-bound and void gases. *Geochim. Cosmochim. Acta* 69 (4), 1007–1026.
- Moridis, G.J., Collett, T.S., Boswell, R., Hancock, S., Rutqvist, J., Santamarina, C., Kneafsey, T., Reagan, M.T., Pooladi-Darvish, M., Kowalsky, M., 2013. Gas Hydrates as a Potential Energy Source: State of Knowledge and Challenges, Advanced Biofuels and Bioproducts. Springer, pp. 977–1033.
- Murshed, M.M., Klapp, S.A., Enzmann, F., Szeder, T., Huthwelker, T., Stapanoni, M., Marone, F., Hintermüller, C., Bohrmann, G., Kuhs, W.F., 2008. Natural gas hydrate investigations by synchrotron radiation X-ray cryo-tomographic microscopy (SRXCTM). *Geophys. Res. Lett.* 35 (23).
- Paganoni, M., Cartwright, J., Foschi, M., Rensbergen, P.V., Shipp, C., 2016. Structure II gas hydrates found below the bottom simulating reflector. *Geophys. Res. Lett.* 43 (11), 5696–5706.
- Paganoni, M., Cartwright, J.A., Foschi, M., Shipp, C.R., Rensbergen, P.V., 2017. Relationship between fluid-escape pipes and hydrate distribution in offshore Sabah (NW Borneo). *Mar. Geol.* 395 (1), 82–103.
- Pape, T., Bahr, A., Rethemeyer, J., Kessler, J.D., Sahling, H., Hinrichs, K.U., Klapp, S.A., Reeburgh, W.S., Bohrmann, G., 2010. Molecular and isotopic partitioning of low-molecular-weight hydrocarbons during migration and gas hydrate precipitation in deposits of a high-flux seepage site. *Chem. Geol.* 269 (3), 350–363.
- Pape, T., Bahr, A., Klapp, S.A., Abegg, F., Bohrmann, G., 2011. High-intensity gas seepage causes rafting of shallow gas hydrates in the southeastern Black Sea. *Earth Planet. Sci. Lett.* 307 (1), 35–46.
- Pinero, E., Marquardt, M., Hensen, C., Haeckel, M., Wallmann, K., 2013. Estimation of the global inventory of methane hydrates in marine sediments using transfer functions. *Biogeosciences* 10 (2), 959–975.
- Plaza-Faverola, A., Bünnz, S., Mienert, J., 2011. Repeated fluid expulsion through sub-seabed chimneys offshore Norway in response to glacial cycles. *Earth Planet. Sci. Lett.* 305 (3–4), 297–308.
- Plaza-Faverola, A., Vadakkupuliyambatta, S., Hong, W.L., Mienert, J., Bünnz, S., Chand, S., Greinert, J., 2017. Bottom-simulating reflector dynamics at Arctic thermogenic gas provinces: an example from Vestnesa Ridge, offshore west-Svalbard. *J. Geophys. Res.* 122.
- Priest, J.A., Druce, M., Roberts, J., Schultheiss, P., Nakatsuka, Y., Suzuki, K., 2015. PCATS Triaxial: a new geotechnical apparatus for characterizing pressure cores from the Nankai Trough. *Jpn. Times: Mar. Petrol. Geol.* 66 (Part 2), 460–470.
- Qian, J., Wang, X., Collett, T.S., Guo, Y., Kang, D., Jin, J., 2018. Downhole log evidence for the coexistence of structure II gas hydrate and free gas below the bottom simulating reflector in the South China Sea. *Mar. Petrol. Geol.* 98, 662–674.
- Rehder, G., Brewer, P.W., Peltzer, E.T., Friederich, G., 2002. Enhanced lifetime of methane bubble streams within the deep ocean. *Geophys. Res. Lett.* 29 (15), 21–21–21–24.
- Sassen, R., Macdonald, I.R., 1994. Evidence of structure H hydrate, Gulf of Mexico continental slope. *Org. Geochem.* 23 (6), 1029–1032.
- SASSEN, Joye, S.T., Defreitas, D., Milkov, A., V.A., 1999. Thermogenic gas hydrates and hydrocarbon gases in complex chemosynthetic communities, Gulf of Mexico continental slope. *Org. Geochem.* 30 (7), 485–497.
- Sassen, R., Losh, S.L., Iii, L.C., Roberts, H.H., Whelan, J.K., Milkov, A.V., Sweet, S.T., Defreitas, D.A., 2001. Massive vein-filling gas hydrate: relation to ongoing gas migration from the deep subsurface in the Gulf of Mexico. *Mar. Petrol. Geol.* 18 (5), 551–560.
- Sassen, R., Sweet, S.T., Milkov, A.V., Defreitas, D.A., Kennicutt, M.C., Roberts, H.H., 2013. Stability of thermogenic gas hydrate in the Gulf of Mexico: constraints on models of climate change. *Washington Dc American Geophysical Union Geophysical Monograph* 124, 131–143.
- Sha, Z., Liang, J., Zhang, G., Yang, S., Lu, J., Zhang, Z., McConnell, D.R., Humphrey, G., 2015. A seepage gas hydrate system in northern South China Sea: seismic and well log interpretations. *Mar. Geol.* 366, 69–78.
- Sibuet, M., Olu, K., 1998. Biogeography, biodiversity and fluid dependence of deep-sea cold-seep communities at active and passive margins. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 45 (1–3), 517–567.
- Sloan, E.D., 2003. Fundamental principles and applications of natural gas hydrates. *Nature* 426 (6964), 353–363.
- Sloan Jr., E.D., Koh, C., 2007. Clathrate Hydrates of Natural Gases. CRC press.
- Smith, A.J., Mienert, J., Bünnz, S., Greinert, J., 2014. Thermogenic methane injection via bubble transport into the upper Arctic Ocean from the hydrate-charged Vestnesa Ridge, Svalbard: *Geochim. Geophys. Res.* 15 (5), 1945–1959.
- Solomon, E.A., Kastner, M., Jannasch, H., Robertson, G., Weinstein, Y., 2008. Dynamic fluid flow and chemical fluxes associated with a seafloor gas hydrate deposit on the northern Gulf of Mexico slope. *Earth Planet. Sci. Lett.* 270 (1–2), 95–105.
- Sultan, N., Bohrmann, G., Ruffine, L., Pape, T., Riboulot, V., Colliat, J.L., De Prunel, A., Dennielou, B., Garziglia, S., Himmler, T., 2014. Pockmark formation and evolution in deep water Nigeria: rapid hydrate growth versus slow hydrate dissolution. *J. Geophys. Res.: Solid Earth* 119 (4), 2679–2694.
- Torres, M.E., Wallmann, K., Tréhu, A.M., Bohrmann, G., Borowski, W.S., Tomaru, H., 2004. Gas hydrate growth, methane transport, and chloride enrichment at the southern summit of Hydrate Ridge, Cascadia margin off Oregon. *Earth Planet. Sci. Lett.* 226 (1–2), 225–241.
- Torres, M., Tréhu, A.M., Cespedes, N., Kastner, M., Wortmann, U., Kim, J.-H., Long, P., Malinverno, A., Pohlman, J., Riedel, M., 2008. Methane hydrate formation in turbidite sediments of northern Cascadia. *Earth Planet. Sci. Lett.* 271 (1), 170–180 IODP Expedition 311.
- Torres, M., Collett, T., Rose, K., Sample, J., Agena, W., Rosenbaum, E., 2011a. Pore fluid geochemistry from the Mount Elbert gas hydrate stratigraphic test well, Alaska North Slope. *Mar. Petrol. Geol.* 28 (2), 332–342.
- Torres, M.E., Kim, J.-H., Choi, J.-Y., Ryu, B.-J., Bahk, J.-J., Riedel, M., Collett, T.S., Hong, W.-L., Kastner, M., 2011b. Occurrence of high salinity fluids associated with massive near-seafloor gas hydrate deposits. In: Proceedings 7th International Conference on

- Gas Hydrates (ICGH 2011).
- Tréhu, A.M., Long, P.E., Torres, M.E., Bohrmann, G., Rack, F.R., Collett, T.S., Goldberg, D.S., Milkov, A.V., Riedel, M., Schultheiss, P., Bangs, N.L., Barr, S.R., Borowski, W.S., Claypool, G.E., Delwiche, M.E., Dickens, G.R., Gracia, E., Guerin, G., Holland, M., Johnson, J.E., Lee, Y.J., Liu, C.S., Su, X., Teichert, B., Tomaru, H., Vanneste, M., Watanabe, M., Weinberger, J.L., 2004. Three-dimensional distribution of gas hydrate beneath southern Hydrate Ridge: constraints from ODP Leg 204. *Earth Planet. Sci. Lett.* 222 (3–4), 845–862.
- Wang, X., Wu, U. S., Yuan, S., Wang, D., M. A. Y., Yao, G., Gong, Y., Zhang, G., 2010. Geophysical signatures associated with fluid flow and gas hydrate occurrence in a tectonically quiescent sequence. Qiongdongnan Basin, South China Sea: *Geofluids* 10 (3), 351–368.
- Wang, X., Hutchinson, D.R., Wu, S., Yang, S., Guo, Y., 2011. Elevated gas hydrate saturation within silt and silty clay sediments in the Shenhu area, South China Sea. *J. Geophys. Res.: Solid Earth* 116 (B5), B05102.
- Wei, J., Pape, T., Sultan, N., Colliat, J.-L., Himmler, T., Ruffine, L., De Prunele, A., Dennielou, B., Garziglia, S., Marsset, T., 2015. Gas hydrate distributions in sediments of pockmarks from the Nigerian margin—Results and interpretation from shallow drilling. *Mar. Petrol. Geol.* 59, 359–370.
- Wei, J., Fang, Y., Lu, H., Lu, H., Lu, J., Liang, J., Yang, S., 2018. Distribution and Characteristics of Natural Gas Hydrates in the Shenhu Sea Area. *Marine and Petroleum Geology*, South China Sea.
- Weinberger, J.L., Brown, K.M., 2006. Fracture networks and hydrate distribution at Hydrate Ridge, Oregon. *Earth Planet. Sci. Lett.* 245 (1), 123–136.
- Weinberger, J.L., Brown, K.M., Long, P.E., 2005. Painting a picture of gas hydrate distribution with thermal images. *Geophys. Res. Lett.* 32 (4).
- Wu, T., Sahling, H., Feseker, T., Rendle-Bühning, R., Wei, J., Wintersteller, P., Marcon, Y., Pape, T., Römer, M., Bohrmann, G., 2019. Morphology and activity of the helgoland mud volcano in the sorokin trough, northern black sea. *Mar. Petrol. Geol.* 99, 227–236.
- Zhang, G., Liang, J., Lu, J. a., Yang, S., Zhang, M., Holland, M., Schultheiss, P., Su, X., Sha, Z., Xu, H., 2015. Geological features, controlling factors and potential prospects of the gas hydrate occurrence in the east part of the Pearl River Mouth Basin, South China Sea. *Mar. Petrol. Geol.* 67, 356–367.
- Zhang, G., Zeng, Q., Long, S., Yang, H., Ying, C., Yang, D., Mo, J., Chengfu, L., Sun, Y., 2016. Accumulation mechanism of LS 17-2 deep water giant gas field in Qiongdongnan Basin. *Acta Pet. Sin.* 37, 34–46.
- Zhang, W., Liang, J., Su, P., Wei, J., Gong, Y., Lin, L., Liang, J., Huang, W., 2018. Distribution and characteristics of mud diapirs, gas chimneys, and bottom simulating reflectors associated with hydrocarbon migration and gas hydrate accumulation in the Qiongdongnan Basin, northern slope of the South China Sea. *Geol. J.* 0 (0).
- Zhao, Z., Sun, Z., Wang, Z., Sun, Z., Liu, J., Zhang, C., 2015. The high resolution sedimentary filling in Qiongdongnan Basin, northern South China sea. *Mar. Geol.* 361, 11–24.